Influence of the form of photodeposited platinum on titania upon its photocatalytic activity in CO and acetone oxidation

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Abstract

Specimens of titania with platinum in various oxidation states deposited by a photocatalytic method, as well as mixture of $PtO_2 + TiO_2$, and PtO_2 have been studied by means of XPS, TEM and UV-VIS diffuse reflectance spectroscopy. Activities of the specimens in thermal and photocatalytic complete oxidation of gaseous acetone and CO by atmospheric oxygen at 40°C have been evaluated using a flow-circulating reactor. Photocatalytic activity increases with lowering of Pt oxidation state. Possible reasons of this behavior are discussed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Photocatalytic reactions have recently attracted much attention because of their ability to proceed at a substantial rate under ambient conditions. The search for active photocatalysts has revealed that platinized titania is a very active catalyst for a lot of photocatalytic reactions. This photocatalyst has been used for oxidative reactions in gaseous [1–5] and liquid phase [6,7], reduction [8,9], water decomposition [10–13] hydrogenation [14], dehydrogenation [15–18], photo-Kolbe reactions [19–21], deuterium isotopic exchange [22,23] and cyclization of amino acid [24]. Many of these studies [7–10,12,13,16,18–20] used platinized titania prepared by photocatalytic deposition of platinum.

In previous papers [25,26] it has been reported that the photocatalytic deposition of Pt from H_2PtCl_6 solution proceeds through the formation of hydrolysis products. Different pH values and different concentrations of acetic acid during the photocatalytic deposition can result in different platinum deposit forms. Generally, increase in pH leads to the deposit having a higher platinum oxidation state, but increase in acetic acid concentration has the reverse effect.

This work is aimed at elucidation how various forms of photocatalytically deposited platinum influence titania activity in oxidation of gaseous compounds such as acetone and CO.

2. Experimental

The procedure of platinum photocatalytic deposition on TiO_2 based on previous results [26] was as follows. 2 g of TiO_2 (Fluka AG), 1.32 ml of 0.077 M H_2PtCl_6 and estimated quantity of 0.1 M acetic acid were mixed to give total volume 20 ml. Specimen A was prepared with addition of water instead of acetic acid. The suspensions formed were brought to the required pH by addition of NaOH solution. The pH values for specimens A, B and C were 11.95, 12.16 and 3.93, respectively. Oxygen was removed from suspensions by passing high-purity nitrogen for 15 min. Then, the suspensions were illuminated with 250 W mercury lamp. After irradiation, specimens were washed with distilled water until no Cl- was detected in rinsing water. Specimens were filtered and dried in vacuum at 100°C for 2 h.

Specimen D was prepared by high temperature oxidation of H_2PtCl_6 with NaNO3. Specimen E is a mixture of TiO_2 and PtO_2 in proportion 64 : 36 by weight. TiO_2 Fluka AG is designated as specimen F.

UV-VIS diffuse reflectance spectra of the specimens were recorded using Shimadzu UV-300 spectrophotometer (Japan). MgO was a reference specimen and its reflectance was assumed to be 85%.

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X-ray photoelectron spectra were recorded using a PHI-550 multitechnique spectrometer (P–E Co.). Platinum oxidation state and phase composition were ascertained on the basis of information given in [25,26] and references therein.

Photocatalytic activity of specimens was determined in a flow-circulation system described in detail in [27]. This includes a quartz reactor, a membrane circulation pump and stainless steel connection pipes. The circulation rate provided by the pump was about 5 l/min, that is 100 times as high as maximum input flow rate used. Therefore, the reactor can be considered as a perfect stirring reactor and there are no concentration and temperature gradients.

Atmospheric oxygen was used as an oxidant. The input gas flow was prepared according to the following procedure. Purified air was divided into three flows. One was passed through a saturator filled with water to attain the necessary water vapor concentration. For experiments on acetone oxidation the second flow was passed through a saturator with acetone. The third flow was used to dilute the gas mixture after the confluence of all the flows. For experiments on CO oxidation, this compound was added instead of the second flow.

Input and output gas mixtures were analyzed using gas chromatographs equipped with flame ionization detectors and thermal conductivity detector. Carbon dioxide was determined by analyzing methane resulting from methanation of a gas probe.

The specimens of photocatalysts for tests were applied to glass plates from aqueous pastes. The quantity applied was approximately 20 mg for each specimen. The area of the specimens' spot was $3 \, cm^2$ and the thickness of each specimen film was high enough not to transmit the incident light.

Specimens in the quartz reactor were irradiated by the light of 1000 W xenon lamp transmitted through 313 nm interference filter. Incident light intensity was $7 \, mW/cm^2$.

The concentration of water vapor was 4000 ± 300 ppm for all the tests, acetone and CO concentrations were 550 ± 30 ppm and 4200 ± 100 ppm for respective tests of activity.

Quantum yields of CO and acetone oxidation were calculated from the CO_2 formation rate by taking that 2 and 16 photons are necessary to oxidize each molecule of CO and acetone, respectively. The numbers of photons are based on an assumption that two photons are required to form each oxidizing oxygen atom. An analogous approach to the quantum yield calculation has been used by other authors [28–30]. Since nearly all the light with wavelength <350 nm is absorbed by TiO_2 [27], quantum yields were calculated using incident light intensity.

3. Results and discussion

Fig. 1 shows X-ray photoelectron spectra of platinum-containing specimens. A peak with two shoulders for specimen A, as it has been demonstrated in [25], is a result of superposition of two-banded spectra for $Pt(OH)_2$ and PtO_2. Therefore, there are two oxidation states of platinum in comparable quantity in specimen A: two and four. The spectrum of platinum for specimen B is peculiar to $Pt(OH)_2$. No other platinum forms are detectable. Specimen C has spectrum characteristic of metallic platinum. The position of the Pt $4f_{7/2}$ band for specimen D coincides with literature data on PtO_2. In the spectrum for specimen E, the energy of the Pt $4f_{7/2}$ band is slightly higher than the energy for PtO_2 and close to the energy for H_2PtCl_6. A small quantity of Pt^0 is detectable in this specimen. Results of XPS characterization are summarized in Table 1.

Represented in Fig. 2 are fragments of TEM images of specimens under investigation. Particles of TiO_2 (Fluka AG) have diameter ranging from 58 to 300 nm, the average size being near 160 nm. These primary particles form agglomerates of still greater sizes approximating several micrometers. Platinum particles in specimen A seem to be non-uniformly distributed among the TiO_2 particles, and their diameter is approximately 0.8–1.6 nm. It was impossible to determine from photomicrographs whether PtO_2 and $Pt(OH)_2$ constitute different particles or they reside in a mixed state in the same particles.

In specimen B, sizes of platinum particles have wider distribution, approximately from 0.5 to 7 nm with domination of smaller particles. Large particles are often composed of smaller particles bound together. The platinum particles appear to be uniformly distributed among and over the surface of TiO_2 particles.

Specimen C contains non-uniformly distributed Pt particles often forming agglomerates or areas with high density. Distribution of primary particles size is rather narrow and

Table 1
Activity of photocatalysts in acetone and CO photocatalytic oxidation

Specimen	Phase composition	Pt surface relative atomic (%)	Quantum yield in acetone oxidation (%)	Quantum yield in CO oxidation (%)
A	$PtO_2+Pt(OH)_2/TiO_2$	1.2	2.8 (<0.5)	0.9 (<0.2)
B	$Pt(OH)_2/TiO_2$	1.5	5.5 (<0.5)	1.6 (0.9)
C	Pt^0/TiO_2	0.8	33 (1.4)	1.2 (<0.2)
D	PtO_2	29	1.4 (<0.5)	(32)
E	PtO_2/TiO_2	(36 wt.%)	4.2 (<0.5)	(34)
F	TiO_2	–	30 (<0.5)	0.6 (<0.2)

Dark activities in parentheses are given for comparison in the same units as photocatalytic activity.
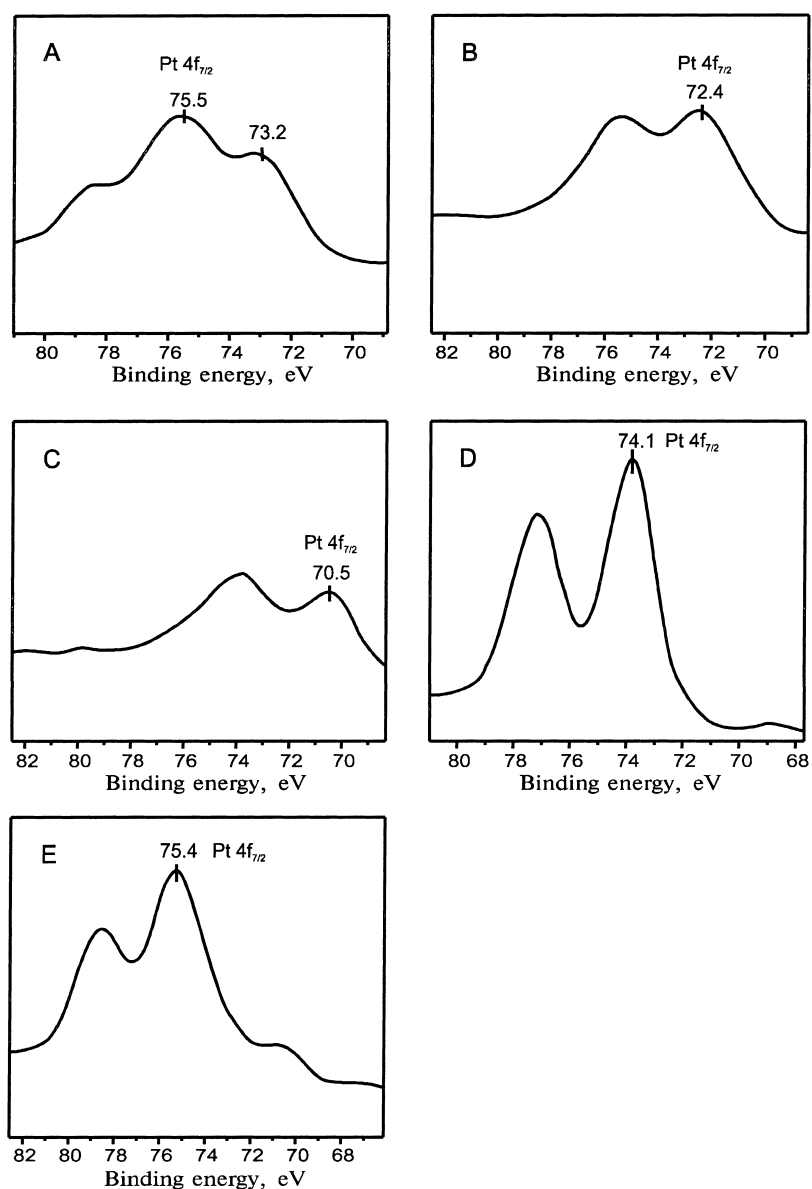
Fig. 1. X-ray photoelectron spectra of platinum in respective specimens.

approximates 3 nm. Agglomeration of particles of Pt resulted probably from thermal treatment of this specimen at 100°C. Thus, no strong interaction with support is observed.

Particles of PtO_2 in specimen D are oblong. Their diameter is about 6 nm and length is approximately 50 nm. Roundish-formed crystallites of diameter 50 nm are also observed.

Specimen E is clearly seen to be a mechanical mixture of titania with particles of 200 nm and platinum dioxide with round particles of size 10–30 nm.

Reflectance of the specimens in UV-VIS is shown in spectra in Fig. 3. Pure titanium dioxide reflects almost all incident visible light and absorbs nearly all ultraviolet light. Specimens with deposited platinum show significant absorption of visible light depending on form of platinum. As the

relative atomic percentages of platinum in specimens A, B and C are close, differences between their spectra are mainly due to form of photodeposited platinum. Indeed, at any wavelength, reflection of specimen C (Pt^0/TiO_2) is approximately half as much as reflection of specimen F (TiO_2), because highly dispersed platinum is known to absorb nearly all the incident light and therefore does not change the shape of the specimen's F spectrum. However, spectrum of specimen A ($PtO_2 + Pt(OH)_2/TiO_2$) cannot be obtained by superposition of those of specimens E (PtO_2), B ($Pt(OH)_2$) and F (TiO_2). Part of the specimen's A spectrum responsible for PtO_2 band gap absorption edge begins to level at substantially shorter wavelength than those of E and B. Possible explanation is that particles of PtO_2 in specimen A are very small, and the quantum-size effect can be observed at these semiconductor particle sizes, shifting absorption edge to
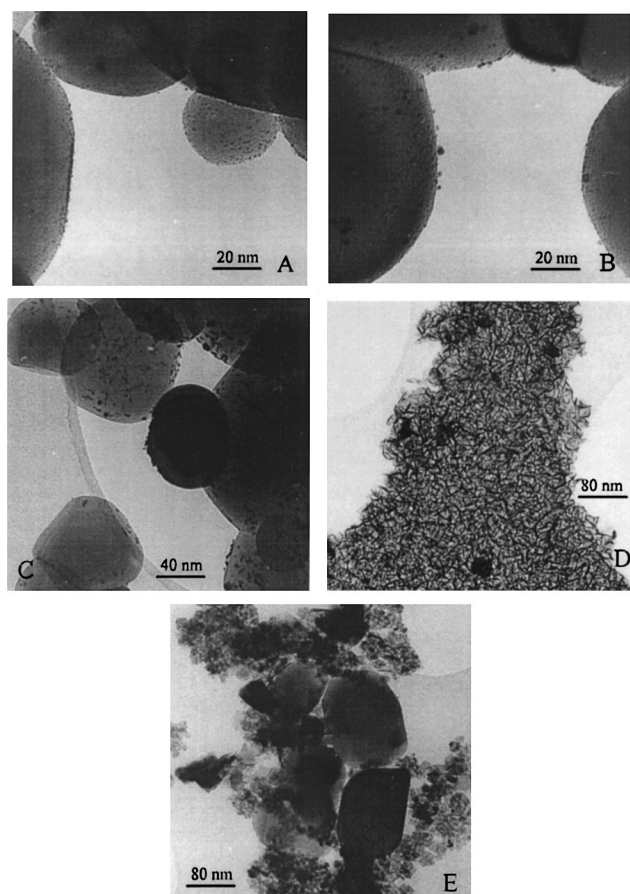
Fig. 2. TEM images of photocatalysts studied.

shorter wavelength. Band gap energy for PtO_2 in specimen A approximates 2.1 eV, in specimen D it is lower than 1.5 eV, as calculated from the band gap absorption edge wavelength. In the literature the band gap of PtO_2 is reported to be 0.2 eV [31].
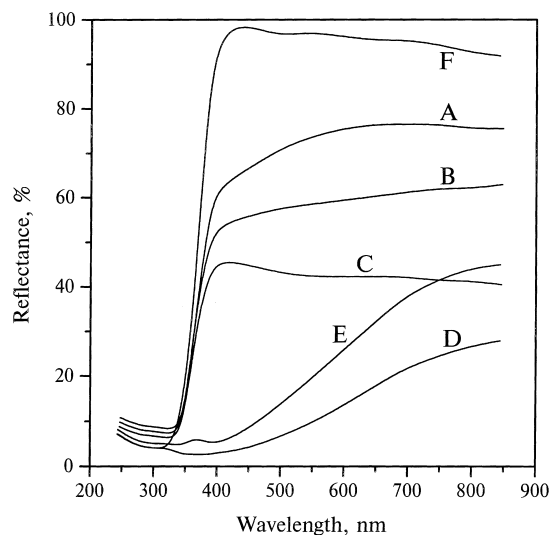

Fig. 3. UV-VIS diffuse reflectance spectra of specimens.

Though low-percentage platinum photodeposits have strong influence on specimens' absorption in visible light, there seems to be small effect on quantity of UV light absorbed by TiO_2. The characteristic depth of UV light penetration into TiO_2 is about some hundreds nanometers, which is close to sizes of TiO_2 particles used. Therefore, platinum particles are able to absorb only the UV light fraction equal to their surface coverage on TiO_2. Since the fraction of TiO_2 surface covered with platinum, as given in Table 1, is about 1% for specimens A, B and C, the presence of platinum deposit do not change appreciably the quantity of UV light absorbed. Specimen E, however, consists of mechanical mixture of titanium and platinum oxides. Therefore, the layer of PtO_2 can be thick enough to absorb a significant part of UV light, and TiO_2 is expected to get only a small part of UV light.

Platinum deposits exert considerable influence on the rate of photocatalytic oxidation of acetone and CO, as illustrated in Table 1. Generally, photocatalytic activity of photoplatinized specimens in acetone oxidation increases with decrease of platinum oxidation state in the photodeposit. Dark oxidation was observed only on Pt^0/TiO_2. Only specimen with Pt^0 has higher activity than pure TiO_2. The decline of activity of the photoplatinized specimens cannot be due to absorption of UV light by platinum, since, as shown above, the fraction of light absorbed by platinum is small. Possible reasons for this low activity include (1) recombination of photogenerated charge carriers in particles of platinum deposit or at platinum deposit–titania interface, (2) modification of titania particles itself during photodeposition procedure, that causes an increased charge carrier recombination rate at the TiO_2 surface, and (3) blockage of active reaction centers on TiO_2 particles by inactive platinum deposit particles.

Slight growth in activity of specimen Pt^0/TiO_2 compared to TiO_2 may be due to a better photogenerated charge separation that decreases the recombination rate. Another explanation for this growth consist in higher reaction rate on platinum particles, where some part of the reaction can take place.

Specimen D (PtO_2) has very poor activity in the acetone oxidation under the given conditions, no reaction being detected in the dark. Thermal nature of this activity cannot be completely excluded, since some heating under light takes place.

Mechanical mixture of TiO_2 and PtO_2 also showed low activity compared to TiO_2. This results from probably predominant consumption of UV light by PtO_2 which covers TiO_2 with rather thick polycrystalline layer.

All the photoplatinized specimens of titania have increased photocatalytic activity for CO oxidation. Specimens A and B have nearly equal photocatalytic activity. Only specimen B has significant thermal activity. Again, the highest photocatalytic activity is in the case of Pt^0/TiO_2. Difference in change of activity of specimens A and B after platinization for CO and acetone oxidation may be attributed

to a thermal oxidation of CO on the platinum particles surface slightly heated by UV light.

Specimens D and E exhibited only thermal CO oxidation. Their activity was gradually developed during several hours, whereas activity of other specimens in both acetone and CO oxidation remained unchanged after first approximately 45 min of reaction. It is reasonable to suppose that CO oxidation proceeds on Pt^0 which is the product of PtO_2 reduction by CO. Therefore, the rate of CO oxidation increases with time of reaction, as the surface of Pt^0 rises. It is surprising that similar behavior was not observed for specimens A and B.

4. Conclusions

Photocatalytic deposition of platinum resulted in nanometer-sized particles on the surface of TiO_2 particles. Titanium dioxide with various forms of photodeposited platinum particles has turned out to have different photocatalytic activity in acetone and CO oxidation. The activity in both oxidation processes rises with decrease of oxidation state of platinum. Only Pt^0/TiO_2 has higher activity than TiO_2 in acetone oxidation, whereas all specimens with platinum showed higher activity in CO oxidation.

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